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Stereoselectivity in the Reaction of Dimethylsulfonium Phenacylide with Dibenzoylethylene

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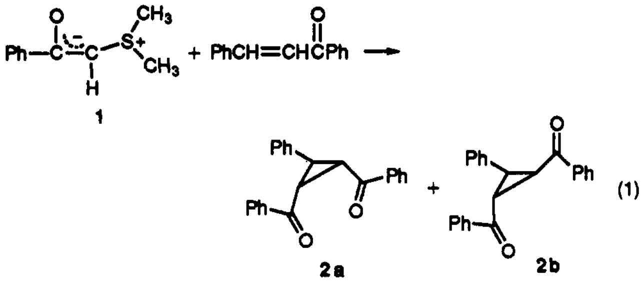
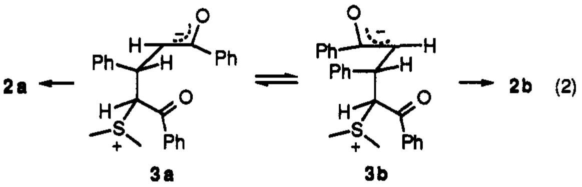
The addition of sulfur and phosphonium ylides to unsaturated carbonyl compounds has been the subject of a number of studies,[1] often with the aim of generating cyclopropanes stereospecifically, e.g., commercially important pyrethrin insecticides. One of the early stereochemical investigations was the addition of dimethylsulfonium phenacylide, **1**, to *trans*-chalcone in benzene at 25 °C giving cyclopropanes **2a** and **2b** in a ratio of 2:1.[2]



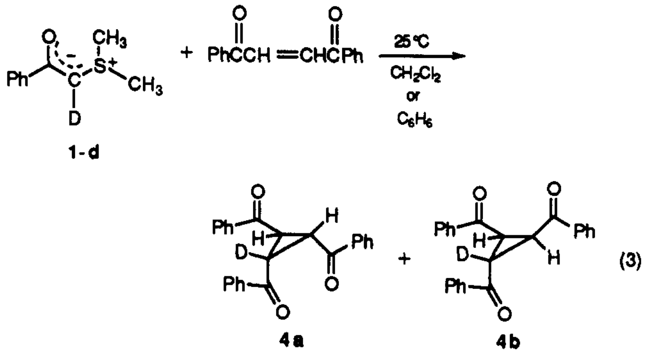
The product distribution, with the less stable **2a** as the major product, was attributed to the greater population of conformation **3a**, which shows fewer nonbonded interactions than **3b**.

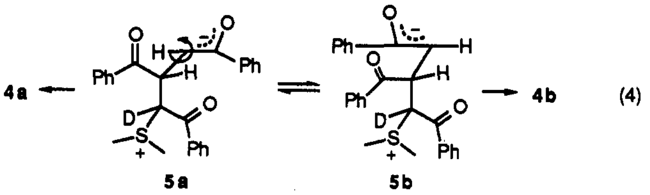


A similar stereochemical result was obtained with substituted chalcones in dichloromethane, in which the only isolated cyclopropanes had benzoyl groups that were *cis*-oriented.[3]

Though cyclopropanation with **1** and dibenzoylethylene has been examined,[2] the stereochemical outcome is not available for comparison with chalcone. To secure this information, for which there seems to be no general predictive rules,[4] we have treated *cis*- and *trans*-dibenzoylethylene with **1**-*d* to give the energetically equivalent *trans*-tribenzoylcyclopropanes **4a** and **4b**.

If there is an appreciable barrier to rotation about the designated carbon–carbon single bond in **5a**, then the expectation might be that **4a** is formed exclusively and that the ^{1}H NMR spectrum of the product should exhibit an AB pattern of two doublets. If there is essentially free rotation about this bond, as with **3**, i.e., the rate of rotation is rapid with respect to the rate of ring closure, the mixture of conformers **5a** and **5b** should lead to a mixture of cyclopropanes **4a** and **4b** dictated by the relative populations of **5a** and **5b** as in the case of chalcone.





The deuterated ylide, **1**-*d*, was prepared from dimethylphenacylsulfonium bromide-d_2, which was obtained by allowing the undeuterated salt to exchange with D_2O. The α-carbon of the precursor to **1**-*d* can be observed in the proton-decoupled ^{13}C spectrum as a five-line pattern centered at 52.6 ppm with $^1J_{^{13}C-^1H} = 17$ Hz indicating that both α hydrogens have been exchanged for deuterium. Long accumulation with long pulse delays (to allow for lack of dipole–dipole relaxation) permitted this observation. The α carbon of the related salt, methylisopropylphenacylsulfonium bromide, was reported to be nonobservable in D_2O due to rapid exchange,[5] but detection of this carbon would seem possible by use of the appropriate pulse pattern.

We find that the ^{1}H NMR spectrum of the product mixture from both *cis*- and *trans*- dibenzoylethylene shows two doublets centered at 4.25 and 3.77 ppm ($J = 5.6$ Hz) and a singlet at 3.77 ppm showing, from the area ratio, a 1:1 mixture of **4a** and **4b**. This nonstereoselectivity in the ring closure step affording **4** is most easily accommodated by assuming that the C_β benzoyl group in **5** is less sterically demanding than the corresponding phenyl group in **3** and does not lead to any conformational preference between **5a** and **5b**.

We also observe the same 1:1 product distribution in both benzene and dichloromethane, which appears to show that this range of solvent polarity, as with the formation of **2** in the same solvents,[2,3] does not influence the stereochemical result.[6,7]

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(1) (a) Chapdelaine, M. J.; Hulce, M. *Org. React.* **1990**, *38*, 225. (b) DeVos, M. J.; Krief, A. *Tetrahedron Lett.* **1983**, *24*, 103. (c) Corey, E. J.; Jautelat, M. *J. Am. Chem. Soc.* **1967**, *89*, 3912.

(2) Trost, B. M. *J. Am. Chem. Soc.* **1967**, *89*, 138.

(3) Reddy, D. B.; Reddy, B. V. R. *Ind. J. Chem.* **1982**, *21B*, 959.

(4) Helmquist, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 4, p 986 and references cited therein.

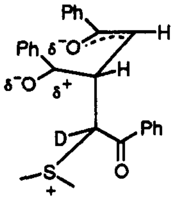
(5) Matsuyama, H.; Minato, H.; Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3393.

(6) While a reviewer suggests that a double labeling experiment would be required to definitively exclude the possibility of intermolecular H–D exchange at C_β, the probability of this process seems minimal, in view of the fact that dideuterated **4** is not seen and that the observed ^{1}H NMR spectrum aromatic/cyclopropyl integration ratio is 15/2.

(7) Cyclization of intermediates related to **3** and **5** has given the less stable cis cyclopropane when the solvent was the nonpolar benzene or toluene. McCoy, L. L. *J. Am. Chem. Soc.* **1962**, *84*, 2246.

0022-3263/93/1958-5853$04.00/0

Alternatively, conformations **5a** and **5b** may be equally populated due to a combination of steric and electronic factors. While **5b** appears analogous to **3b** in the chalcone case, the concentration of **5b** may be increased via the negative charge density on oxygen at the terminal benzoyl interacting with the positive charge density on the carbonyl carbon of the central benzoyl group at C_β as shown below.



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Using the CAChe molecular modeling program,[8] the minimum barriers to rotation about the bond of interest in **3** and **5** were found to be 5.62 and 3.51 kcal/mol, respectively, which seems not to conflict with the above views. The Molecular Mechanics calculations were done on the CAChe WorkSystem, running software version 2.8. The Molecular Mechanics program uses Allinger's MM2 force field,[9] with CAChe augmentations.[10]

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. ^{1}H NMR (90 MHz) and ^{13}C (22.5 MHz) spectra were obtained in $CDCl_3$ and D_2O, using a JEOL FX90Q instrument. The observation of C–D coupling in dimethylphenacylsulfonium bromide-d_2 required an accumulation time of 27.4 h corresponding to 1085 scans with a 91-s pulse delay.

***trans*-Tribenzoylcyclopropane-d_1. Typical Procedure.** To a solution of phenacyldimethylsulfonium bromide (304 mg, 1.17 mmol, prepared from phenacyl bromide and dimethyl sulfide) in 5.0 mL of D_2O in a 15- × 120-mm test tube was added 2.0 mL of a 0.46 M solution of sodium deuteroxide in D_2O. After stirring on a vortex mixer, 2 mL of methylene chloride was added, followed by vigorous mixing. Then *trans*-dibenzoylethylene (175 mg, 0.745 mmol) dissolved in 2 mL of CH_2Cl_2 was introduced. After standing for 20 h at 25 °C, a white solid was seen in the CH_2Cl_2 layer. The aqueous phase was removed, and the solid was filtered at reduced pressure, washed with petroleum ether, and dried in a desiccator. The recovered solid, 179 mg, 68%, mp 210–214 °C, (lit.[2] (nondeuterated) mp 214–216 °C), was examined by ^{1}H NMR spectrometry. Aromatic H/methine H = 15/2.

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[8] CAChe Group, Tektronix, Inc., P.O. Box 500, Beaverton, OR 97077. These computations were made possible by Jack Leahy of CAChe Scientific.

[9] Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

[10] Liu, S.-Y.; Purvis, G. D., III. *CAChe Molecular Mechanics Augmented Force-Field*; Technical Report No. 2, Feb 1990.